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COMPUTER SIMULATION OF A SINGLE POLYMER CHAIN IN DIFFERENT SOLVENTS*

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Abstract In the present paper, the behavior of a single polymer chain under various solvent conditions was modeled by self-avoiding walks (SAW) with nearest neighbors attraction $\Delta\varepsilon$ on a simple cubic lattice. Determination of the θ-condition was based on the numerical results of the mean square radius of gyration and end-to-end distance. It was found that at the θ temperature $\Delta\varepsilon/kT$ equals –0.27. The exponents α in the Mark-Houwink equation with different interaction parameters are consistent with the results of experiments: under θ-condition, $\alpha = 0.5$, and for a good solvent $\alpha = 0.74$–0.84, respectively.

Key word Computer simulation, Self-avoiding walk, Nearest neighbor interaction, Mark-Houwink's exponent

INTRODUCTION

The behavior of a polymer chain under various solvent conditions has been modeled by self-avoiding walks (SAWs) with nearest neighbors (NN) attraction ε ($\varepsilon < 0$) or by self-attracting trails on a lattice. At high temperature (T) the chain is swollen, *i.e.*, its mean square end-to-end distance $<h^2>$ scales with the chain length N as $N^{2\nu}$, where $\nu \approx 0.59$ in three-dimensions[1]. This corresponds to the good solvent regime. As T is decreased (*i.e.*, solvent conditions worsen) the attractions become more effective and at a certain temperature θ (the Flory temperature) they cancel the excluded volume repulsion. So, the chain behaves in many respects like a random walk, *i.e.*, it is characterized by $\nu = 0.5$. At $T < \theta$ the attractions prevail and the chain collapses, *i.e.*, $\nu = 1/3$. This picture is supported by experiments.

In this paper we use Monte Carlo calculations of configurations to generate self-avoiding chains with nearest neighbors (NN) attraction. The values of mean square end-to-end distance $<h^2>$ and mean square radius of gyration $<R^2>$ were computed for a wide range of attractive energies between the non-bonded segments of the chains separated by the lattice spacing. The next section gives the description of calculation method. The remaining sections give the results and their discussion.

METHOD OF SIMULATION

In a dilute polymer solution the interchain interactions are ignored. This means that a polymer solution is modeled as a single self-avoiding walk with interaction between segments and solvents. In our model, for each segment we only consider its nearest-neighbor interactions. The value of $\Delta\varepsilon$ is defined as the energy difference

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for a contact between two separated segments at the nearest neighbor sites on a lattice.

$$\Delta \varepsilon = \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \tag{1}$$

where ε_{11}, ε_{12} and ε_{22} are the energies of interaction associated with solvent-solvent, solvent-segment, segment-segment contacts, respectively. A negative or positive value of $\Delta\varepsilon$ indicates that the polymer chain is in poor or good solvent situation. The total energy of a polymer chain is the sum of all nearest-neighbor energies in its conformation. The energy of the i-th conformation E_i is written as

$$E_i = n_i \times \Delta \varepsilon \tag{2}$$

where n_i is the contact number between the separated segments on the lattice in a chain.

The partition function of a polymer chain is

$$Z = \sum_{i=1}^{\Omega} \exp(-E_i / kT) \tag{3}$$

where Ω is the number of conformations, k is the Boltzmann constant, and T is the absolute temperature. The Boltzmann probability of the i-th conformation is

$$p_i = \exp(-E_i / kT) / Z \tag{4}$$

Therefore the mean square end-to-end distance and the mean square radius of gyration are written as:

$$< h^2 >= \sum_{i=1}^{\Omega} w_i h_i^{\ 2} p_i \tag{5}$$

$$< s^2 >= \sum_{i=1}^{\Omega} w_i h_i^{\ 2} p_i \tag{6}$$

respectively, where w_i is Rosenbluth-Rosenbluth factor[2]. In our simulations, the first step of the walk is placed at the origin of coordinates, before each further step of the walk, each possible direction for the step is examined for avoiding the intersection with previous steps. A list of all directions, which do not cause intersections, is made (called allowed vectors). A random choice of the allowed vectors is made and a step is taken in the chosen direction. After a walk of the desired length is generated, parameters of physical interest for the walk, such as number of nearest-neighbor contacts, mean square end-to-end distance, and mean square radius of gyration, are recorded. To eliminate the difference between computer probability and thermodynamic probability we must separately weight each walk with the Rosenbluth-Rosenbluth method when calculating the averages of parameters over many walks.

NUMERICAL RESULTS AND DISCUSSION

Chain Size and Solvent Quality

Figure 1 shows the dependence of mean square end-to-end distance per unit length on chain length at different $\Delta\varepsilon/kT$. It can be seen that with increasing $\Delta\varepsilon/kT$ the chain is swollen. At $\Delta\varepsilon/kT = -0.27$ the value of $<h^2>/N$ is invariable with increasing chain length, indicating the approach of the θ-state. This value of $\Delta\varepsilon/kT$ at the θ-condition is very close to that obtained by Meirovitch and Lim[3], who gave $\Delta\varepsilon/kT_\theta = -0.274 \pm 0.006$. In θ-state the nearest attraction counteracts the excluded volume repulsion and the chain behaves in many respects like a random walk. With decreasing $\Delta\varepsilon/kT$ the attractions prevail and the chain collapses, *i.e.*, at $\Delta\varepsilon/kT = -0.4$, -0.5, the value of $<h^2>/N$ decreases with increasing chain length (N) and when $N > 450$ the curves become flat which indicates full collapse. In terms of $\Delta\varepsilon/kT$ the solvent can be divided into the following three kinds. When $\Delta\varepsilon/kT > 0$ the solvent is called a good solvent (Fig. 1a). When $0 > \Delta\varepsilon/kT \geq -0.27$and $\Delta\varepsilon/kT < -0.27$ the solvent is called a semi-good solvent and a poor solvent, respectively (Fig.1a and b). In a good solvent, since $<h^2>$ increases with increasing chain length, $<h^2>/N$ was computed with bigger statistical deviations.

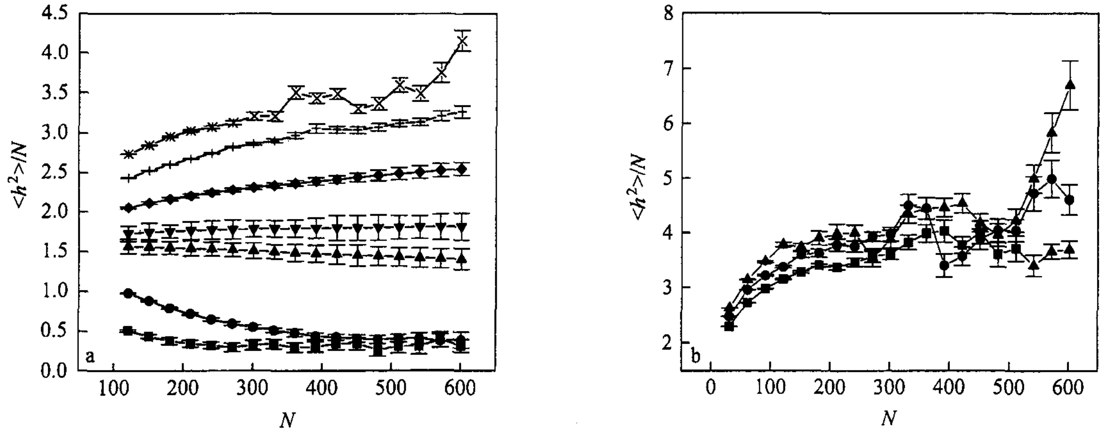

Fig. 1 Mean square end-to-end distance per unit length $<h^2>/N$ plotted versus chain length N for SAW chain with different nearest-neighbor interaction energy $\Delta\varepsilon/kT$ in (a) poor solvent and semi-good solvent and (b) good solvent
a) ■ $\Delta\varepsilon/kT = -0.5$, ● $\Delta\varepsilon/kT = -0.4$, ▲ $\Delta\varepsilon/kT = -0.3$, ▼ $\Delta\varepsilon/kT = -0.27$, ◆ $\Delta\varepsilon/kT = -0.2$, + $\Delta\varepsilon/kT = -0.1$,
× $\Delta\varepsilon/kT = 0$; b) ■ $\Delta\varepsilon/kT = 0.2$, ● $\Delta\varepsilon/kT = 0.4$, ▲ $\Delta\varepsilon/kT = 0.6$

In order to establish a reliable θ-condition, we followed Rubio and co-workers' method[4, 5]. This analysis is a simplified version of the method used by Meirovitch and Lim[6, 7]. The method is based on the expectation that short chains will expand at $T > T_\theta$ with an exponent $\nu > \nu_0$, which increases and approaches ν_0 for very large N. An opposite trend is expected at $T > T_\theta$, where short chains grow with $\nu > \nu_c$ (ν_c is the value of ν at critical point) decreasing to ν_c (for large N). Thus at $T = T_\theta$, ν is expected to become flat, *i.e.*, independent of N, with the value ν_θ. Therefore the θ-point is the point where the data obey the best correlation $R^2 \sim N^{2\nu}$, where ν is constant and equal to 0.5. The curves of $<S^2>/N$ in Fig. 2 show the same results as that in Fig. 1.

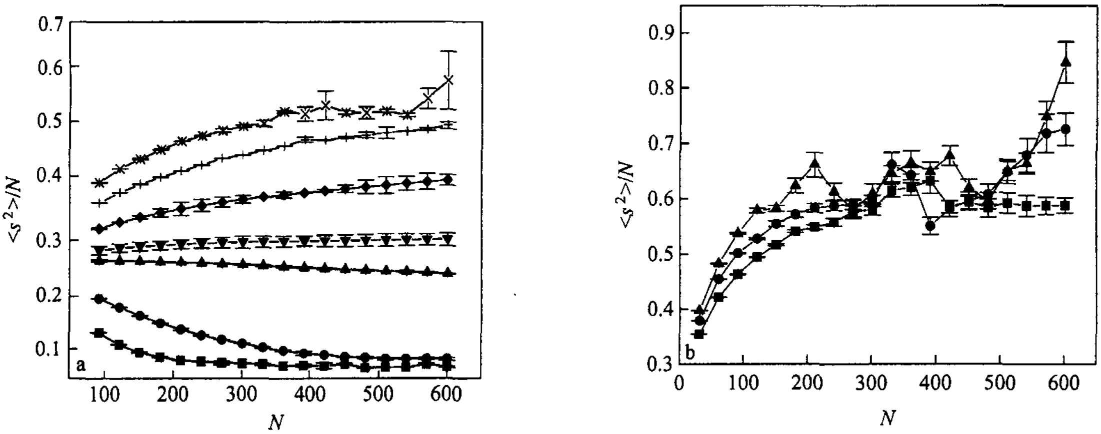

Fig. 2 Mean square radius of gyration per unit length $<S^2>/N$ plotted versus chain length N for SAW chain with different nearest-neighbor interaction energy $\Delta\varepsilon/kT$ in (a) poor solvent and semi-good solvent and (b) good solvent
a) ■ $\Delta\varepsilon/kT = -0.5$, ● $\Delta\varepsilon/kT = -0.4$, ▲ $\Delta\varepsilon/kT = -0.3$, ▼ $\Delta\varepsilon/kT = -0.27$, ◆ $\Delta\varepsilon/kT = -0.2$, + $\Delta\varepsilon/kT = -0.1$,
× $\Delta\varepsilon/kT = 0$; b) ■ $\Delta\varepsilon/kT = 0.2$, ● $\Delta\varepsilon/kT = 0.4$, ▲ $\Delta\varepsilon/kT = 0.6$

Precipitation Phenomenon for Single Chain

On increasing the attractive energy between segments, one might expect the chain to finally collapse upon itself. This phenomenon might be viewed as a single-chain precipitation. We have studied this phenomenon with special interest to ask: (1) if the precipitation occurs over a narrow temperature range as a phase phenomenon? (2) if there is a sharp precipitation, and how it relates to the θ?

Figure 3 shows a plot of S^2/N for various chain lengths vs. $\Delta\varepsilon/kT$. As one goes from small N to larger N there is an increasing steepness in the plot of $\langle S^2\rangle/N$ versus $\Delta\varepsilon/kT$. For N = 571 the steepness of the descent is impressive suggesting that for the long enough chains there is truly a discontinuity of the change rate in radius of gyration corresponding to a precipitation point of the chain, which is in agreement with other investigators[8, 9, 10]. The shape of the curves is in agreement with those obtained from numerical studies[8, 9] and experiments[11].

Inspection of Figs. 3 and 4 suggests that the precipitation point is very close to the θ region. Clearly we need more data as a function of energy around $\Delta\varepsilon/kT$. Suffice it to say here that the data are suggestive but not conclusive proof of single-chain precipitation.

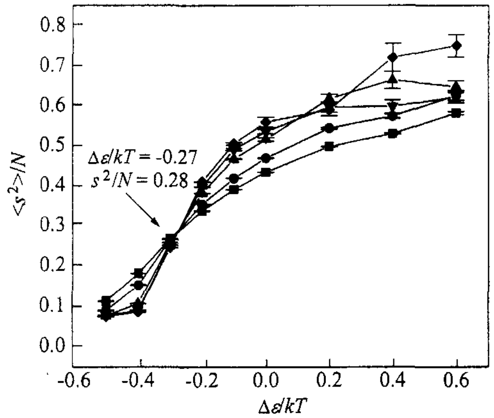

Fig. 3 Mean square radius of gyration per unit length $\langle S^2\rangle/N$ plotted versus nearest-neighbor interaction energy $\Delta\varepsilon/kT$ for SAW chain with different chain length N

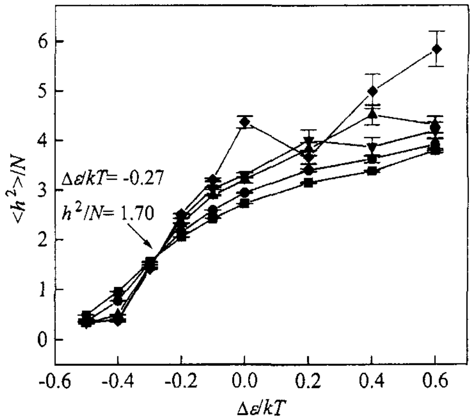

Fig. 4 Mean square end-to-end distance per unit length $\langle h^2\rangle/N$ plotted versus nearest-neighbor interaction energy $\Delta\varepsilon/kT$ for SAW chain with different chain length N

Scaling Analysis of Chain Size

For chains with excluded volume and with attractive energy between unbonded segments, previous workers[12] have found that their $\langle h^2\rangle$ and $\langle R^2\rangle$ data for large chain lengths obeyed

$$\langle R^2\rangle \propto \langle h^2\rangle \propto N^{2\nu} \tag{7}$$

where ν depends on $\Delta\varepsilon/kT$ and at $\Delta\varepsilon/kT = 0$, we have $\nu_0 = 0.59$.

In order to check our results, we plotted $\ln\langle h^2\rangle$ versus $\ln N$ for various $\Delta\varepsilon/kT$ in Fig. 5.

It can be seen that at $\Delta\varepsilon/kT = 0$, -0.2 and -0.27, the plot of $\ln\langle h^2\rangle$ versus $\ln N$ gives straight lines. For $N > 300$, at $\Delta\varepsilon/kT = 0.2$, 0.6 and 1, the graph is no longer straight; this should be due to the statistical error. In Table 1 results for ν are presented at different $\Delta\varepsilon/kT$, where the value of $\nu = 0.5$ predicted by theory is found to occur at $\Delta\varepsilon/kT = -0.27$. At $\Delta\varepsilon/kT = 0$, the value of ν is 0.6, which is in agreement with the theoretical value. For larger attraction ($\Delta\varepsilon/kT = -0.4$ and -0.5), $\langle R^2\rangle$ and $\langle h^2\rangle$ could not be fitted by Eq. (3), *i.e.*, the curves in Fig. 5 did not have a linear range in the range of computed values. Therefore we conclude that the scaling law does not fit $\langle R^2\rangle$ and $\langle h^2\rangle$ for larger attractive energy.

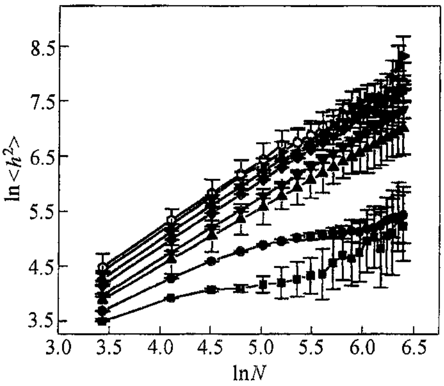

Fig. 5 Log-log plot of mean square end-to-end distance $\langle h^2\rangle$ as a function of chain length N for SAW with different nearest neighbor interaction energy $\Delta\varepsilon/kT$
■ $\Delta\varepsilon/kT = -0.5$, ● $\Delta\varepsilon/kT = -0.4$, ▲ $\Delta\varepsilon/kT = -0.27$, ▼ $\Delta\varepsilon/kT = -0.2$, ◆ $\Delta\varepsilon/kT = 0$, ◀ $\Delta\varepsilon/kT = 0.2$, ▶ $\Delta\varepsilon/kT = 0.6$, ○ $\Delta\varepsilon/kT = 1$

Table 1. The exponent ν of the scaling law $\langle h^2\rangle \propto \langle s^2\rangle \propto N^{2\nu}$ as a function of nearest-neighbor interaction energy $\Delta\varepsilon/kT$

$\Delta\varepsilon/kT$	ν	$\Delta\varepsilon/kT$	ν
−0.27	0.50	0	0.60
−0.25	0.53	0.2	0.58
−0.2	0.57	0.4	0.58
−0.1	0.59	0.6	0.62

Determination of Exponent (α) in the Mark-Houwink Equation

In general, the relationship between intrinsic viscosity $[\eta]$ and average molecular weight M for polymers can be obtained in several ways. One of them is from the Mark-Houwink equation:

$$[\eta] = AM^{\alpha} \tag{8}$$

where A is a constant. The others are from the simplified Flory-intrinsic viscosity equation:

$$[\eta] = \Phi(h^2)^{3/2}/M \tag{9}$$

where Φ is a constant and M is the molecular weight. Here, it is noted that M is directly proportional to the chain length (N). Thus,

$$\alpha = 3\nu - 1 \tag{10}$$

can be obtained from Eqs. (7), (8) and (9). In Table 2 the Mark-Houwink exponent has been calculated with Eq. (8) for a range of interaction parameter from −0.3 to 0.6. At $\Delta\varepsilon/kT = -0.27$ the value of α is 0.5, and at $\Delta\varepsilon/kT = -0.25 - 0.6$ the value of α is in the range from 0.7 to 0.8, which is in agreement with the results obtained from experiments[13]. For the chains of large attractive energy (in poor solvent), accurate values of α can not be obtained. Figure 6 gives the plot of α versus $\Delta\varepsilon/kT$. It can be seen that there is an increasing steepness in Fig. 6 with the variance of $\Delta\varepsilon/kT$ from −0.3 to 0. With can increasing $\Delta\varepsilon/kT$ (from 0 to 0.6), the values of α fluctuate near 0.8 which is the value of α at the infinite temperature condition. Thus, we conclude that it is correct to describe the chain size in good solution with the values of chain size at infinite temperature.

Table 2. Exponent α in Mark-Houwink equation as a function of nearest neighbor interaction energy $\Delta\varepsilon/kT$

$\Delta\varepsilon/kT$	−0.27	−0.25	−0.20	−0.1	0	0.2	0.4	0.6
α	0.50	0.59	0.71	0.77	0.80	0.74	0.74	0.84

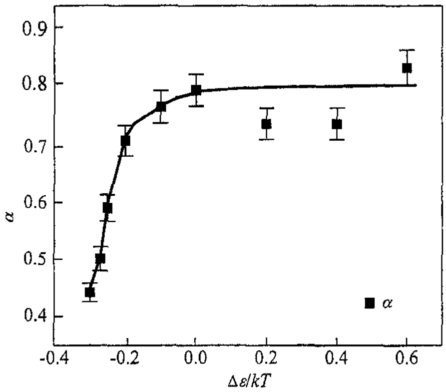

Fig. 6 Exponent α in Mark-Houwink equation plotted versus nearest-neighbor interaction energy $\Delta\varepsilon/kT$

SUMMARY

We have studied the properties of polymer chains in solution at the limit of infinite dilution by SAW with nearest-neighbor attractions on a simple cubic lattice. The θ-point is $\Delta\varepsilon/kT = -0.27$ for such a modeling chain. The results for the mean square radius of gyration, $<R^2>$, and the mean square end-to-end distance, $<h^2>$, are consistent with the scaling equation, in which the exponent value $\nu = 0.5$ at the θ-point. The values for the Mark-Houwink exponent α obtained from the computed exponents ν are in accordance with the results obtained from experiments. Therefor the results obtained by this nearest-neighbor attraction model are in agreement with the properties of real polymers in solution.

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